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Fractal Analysis of the Crystal Surfaces of Calcium 4B Toner Pigments

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ABSTRACT

A method is proposed for the fractal analysis of the crystal surfaces of a wide range of calcium 4B toner pigments, previously characterised by McKay [FATIPEC Congr. XVIII, ***2B*** *(1986), 405]. It is concluded that the crystal surfaces of all but two of the pigments are very smooth. Values for the degree of face-to-face packing of the pigment crystals have been determined from the fractal analysis. These values generally agree closely with the values obtained by McKay's method. © 1997 Elsevier Science Ltd*

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INTRODUCTION

In previous papers,[1,2] the fractal approach to the surface geometry of solids, initiated by Avnir *et al.*,[3–6] has been progressively developed for studying the surfaces of pigment crystals. The fractal approach imposes a dimensional scale, D, on a solid surface, such that $2 \leq D < 3$. Thus, for an ideally smooth surface, which can be treated as perfectly two-dimensional, $D = 2$, whereas for an irregular surface, the value of D lies between 2 and 3.

A surface must exhibit self-similarity[3,4] if it is to be correctly described in terms of a fractal dimension, D: the same type of geometric features can be identified either at different magnifications or where probes of different sizes are used to examine the solid surface. Very many examples of the determination of fractal dimensions for the surfaces of a wide range of solids have been published.[4] One common approach is to utilise the same adsorbate, often nitrogen, on a family of related solid adsorbents. In this approach, the specific surface areas, S_{BET}, of the adsorbents, determined from adsorption isotherms by means of the Brunauer–Emmett–Teller (BET) equation,[7] are analysed as a function of their particle sizes,[4] usually determined from electron micrographs. If the adsorbent surfaces are fractal, then $S_{BET} \propto d^{D-3}$. A plot of log S_{BET} against log d is linear, with a gradient of $(D-3)$. If the particles are highly disperse, however, their size distribution should be taken into account, and a more complex relation between S_{BET} and d emerges.[8]

In practice, the particles of pigments and many other types of solid are anisotropic. Calcium 4B toner pigments, for example, consist of thin, plate-like crystals, and McKay has published extensive data on the crystals of 31 toners, prepared both in the laboratory and on the plant.[9] All but four of the pigments he characterised were coated with a resin, incorporated to control pigment crystal size during preparation and to promote dispersibility in application media.

For each sample of calcium 4B toner pigment, McKay determined the thickness, t, of its constituent crystals, their cross-sectional area, A, and (on the assumption that the resin coats the crystal surfaces uniformly) the thickness, x, of the resin coating, as illustrated in Fig. 1. Thus, the thickness of the coated crystals becomes $(t+2x)$ and the mean dimension across the crystals is $(A^{\frac{1}{2}} + 2x)$. McKay also compared S_{BET} with the geometric surface area, S_c, calculated from the crystal dimensions. The ratio, S_{BET}/S_c, indicates the

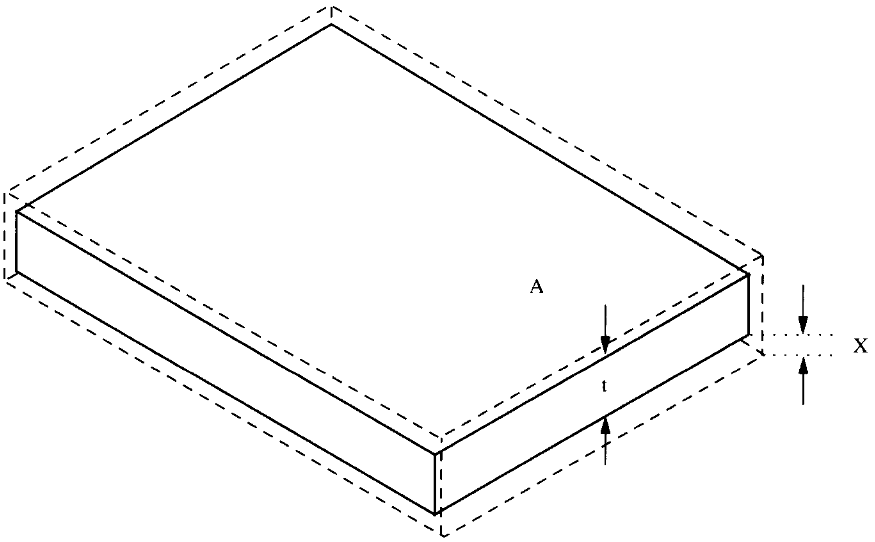

Fig. 1. A schematic representation of a calcium 4B toner pigment crystal, coated uniformly with a layer of resin. A—cross-sectional area of the crystal; t—thickness of the crystal; x—thickness of the resin coating.

extent of face-to-face packing of the pigment crystals. Where $S_{\mathrm{BET}}/S_{\mathrm{c}}$ for a pigment sample is about unity, the crystals form open aggregate structures, largely free of face-to-face contact. Values of $S_{\mathrm{BET}}/S_{\mathrm{c}}$ considerably below unity indicate a more closely packed aggregate structure with substantial face-to-face packing.

In a previous paper,[1] fractal analysis was attempted in terms of crystal thickness and cross-sectional area, separately. Whilst successful in terms of crystal thickness $(t+2x)$, the analysis was far less clear-cut with respect to the mean cross-section $(A^{\frac{1}{2}}+2x)$. It was suggested that there may be substantial variation across the main faces of the pigment crystals.

In a recent paper,[2] an alternative approach has been offered to allow for anisotropy in particles, and has been successfully applied to published data for precursors of iron oxide pigments[10] and for β-copper phthalocynaine pigments.[11] The crystals of these types of pigments appear cylindrical or brick-shaped. In this paper, an analogous approach is applied to McKay's data for calcium 4B toner pigments, which consist of plate-like crystals.

THE METHOD

The area, A, of the surface of each particle in a solid sample scales with average cross-sectional dimension, $2R$, of the particle according to:

$$A \propto R^{D} \tag{1}$$

where D is the fractal dimension of the surface.[4] Thus, the area, A, may be related to the calculated geometric surface area, A_{g} by:

$$A \propto A_{g}^{\frac{D}{2}} \tag{2}$$

since A_{g} is directly proportional to R^2. The specific surface area, S_{S}, of the particle is A/m, where m is the mass of the particle. Therefore:

$$S_S = A/m = A/(\rho V) \tag{3}$$

where V is the volume of the particle and ρ is its density. Expressions (2) and (3) may then be combined, so that:

$$S_S \propto A_g^{\frac{D}{2}}/V,$$

since ρ is a constant.

The specific surface areas of the calcium 4B toner pigments were determined experimentally as S_{BET}.[9] If we consider A_g to be the mean value for the geometric surface area of the particles in a given pigment sample:

$$S_{BET} \propto A_g^{\frac{D}{2}}/V \tag{4}$$

Expression (4) can then be applied to the adsorption of a particular adsorbate, such as nitrogen, on the surfaces of a series of related solids, provided the surfaces exhibit self-similarity.

For a crystal in a sample of calcium 4B toner, as depicted in Fig. 1:

$$A_g = 4(A^{\frac{1}{2}} + 2x)(t + 2x) + 2(A^{\frac{1}{2}} + 2x)^2$$

and:

$$V = (A^{\frac{1}{2}} + 2x)^2(t + 2x)$$

Thus:

$$S_{BET} \propto \frac{[4(A^{\frac{1}{2}} + 2x)(t + 2x) + 2(A^{\frac{1}{2}} + 2x)^2]^{\frac{D}{2}}}{(A^{\frac{1}{2}} + 2x)^2(t + 2x)} \tag{5}$$

Expression (5) may be modified:

$$S_{BET} \cdot (A^{\frac{1}{2}} + 2x)^2(t + 2x) \propto [4(A^{\frac{1}{2}} + 2x)(t + 2x) + 2(A^{\frac{1}{2}} + 2x)^2]^{\frac{D}{2}} \tag{6}$$

A log-log plot of expression (6) would then give a straight line of gradient, $D/2$.

APPLICATION OF THE METHOD

A log-log plot of expression (6) taken from McKay's data is shown in Fig. 2. The theory outlined in the previous section is valid strictly just for those pigments in which there is no face-to-face packing of the crystals, but for only three of the pigments did McKay determine a value of $S_{\mathrm{BET}}/S_{\mathrm{c}}$ equal to unity.[9] The points ● in Fig. 2 corresponding to these pigments are quite close together, so that a linear plot cannot be reliably drawn through them. However, two other groups of pigments for which $S_{\mathrm{BET}}/S_{\mathrm{c}}$ is only slightly below unity may be considered instead: the three pigments represented by the

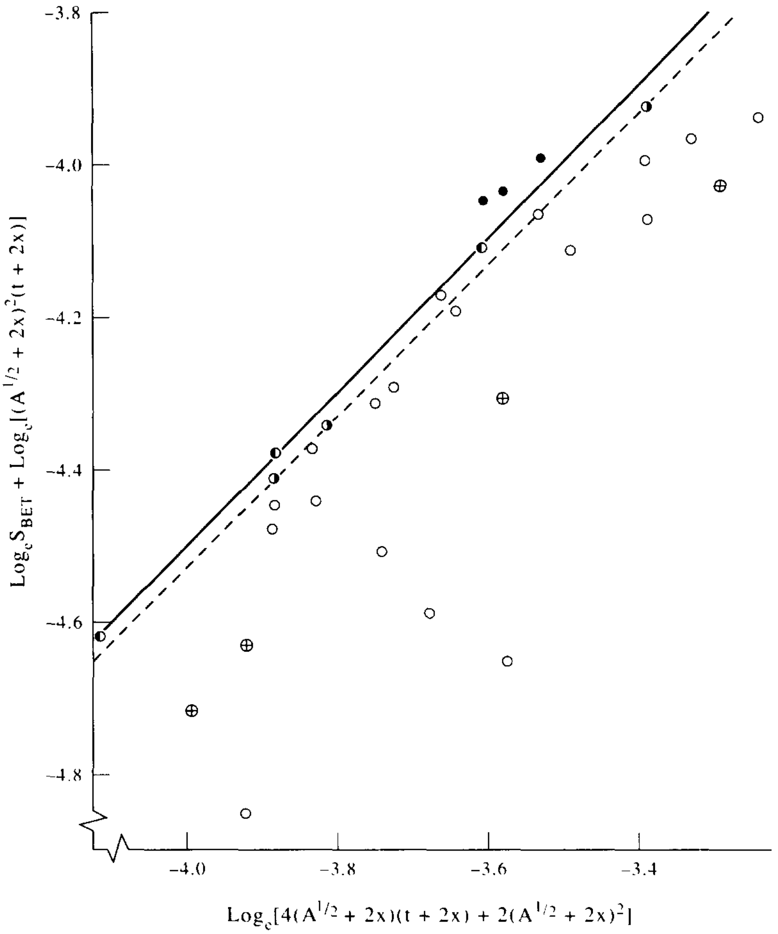

Fig. 2. A fractal plot for calcium 4B toner pigments. The data are plotted according to expression (6).

points ◖ in Fig. 2 ($S_{BET}/S_c = 0.96$), and the three pigments represented by the points ◗ ($S_{BET}/S_c = 0.93$). The crystals of these pigments are aggregated through face-to-face packing to only a small extent. For both groups of pigments, the points are much more widely spread and can be fitted very well by straight lines of gradients very close to unity. The fractal dimensions derived from the lines are 2.01 ± 0.01 and 1.99 ± 0.01, respectively, and may, therefore, be taken as being equal to 2. The surfaces of the crystals in both groups of pigments appear to be very smooth, a consequence perhaps of the resin coating. Moreover, these values correspond well to the fractal dimension, 2.05 ± 0.06, when S_{BET} is monitored solely in terms of the thickness $(t + 2x)$.[1]

It is noteworthy too that the points ⊕ in Fig. 2 corresponding to four pigments for which $S_{BET}/S_c = 0.75$–0.77 are also well fitted by a straight line. The crystals of these pigments are far more severely aggregated. The fractal dimension calculated from the line (gradient 0.98) is 1.96 ± 0.03. This group of pigments was highlighted previously, where a fractal dimension of 1.82 ± 0.15 was determined in terms of pigment crystal thickness. The fractal dimension, 1.96 ± 0.03, is thus close to those determined for the less aggregated pigment samples.

DEGREE OF CRYSTAL AGGREGATION

The position of a point in Fig. 2 corresponding to a pigment with aggregated crystals may be compared with the position expected if the pigment crystals were completely unaggregated. However, as has been observed, there is no reliable linear plot in Fig. 2 corresponding to unaggregated pigments. Instead, the line corresponding to pigments for which $S_{BET}/S_c = 0.96$ may be adopted as a reference line. For each pigment, the expected position of the point on the reference line is found for the value of the abscissa in the log-log plot. The difference in the y-coordinates of the actual and expected position of the points is $\log_e(S_{BET}/S_{ref})$, where S_{ref} would be the specific surface area of the crystals calculated from the reference line. Multiplication of S_{BET}/S_{ref} by 0.96 gives a value for S_{BET}/S_u, where S_u would be the specific surface area of the crystals in an unaggregated state. S_{BET}/S_u may also be similarly calculated using, as a reference line, the line corresponding to pigments for which $S_{BET}/S_c = 0.93$. For every pigment, the values of S_{BET}/S_u determined from the two reference lines differ by no more than 0.01.

S_{BET}/S_u provides a measure of the degree of pigment crystal aggregation, which may be usefully compared with the corresponding value of S_{BET}/S_c calculated by McKay.[9] It should be noted that S_u takes into account the roughness (where it exists) of the pigment crystal surfaces, whereas S_c does not. For only two out of the 31 pigments which McKay studied are there differences greater than 0.01 between S_{BET}/S_u and S_{BET}/S_c. For these two pigments, samples 8 and 17 in McKay's paper,[9] S_{BET}/S_u is less than S_{BET}/S_c by 0.05; thus S_u exceeds S_c.

The agreement between S_{BET}/S_u and S_{BET}/S_c observed for most of the pigments is not unexpected. From the fractal dimensions determined ($D = 2$), it appears that the crystal surfaces are smooth, and McKay[9] implicitly assumed smooth crystal surfaces in his determinations of S_c. By contrast, the crystal surfaces of the two pigment samples, 8 and 17, for which $S_u > S_c$, appear not to be completely smooth.

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